PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-270240

(43)Date of publication of application : 14.10.1997

(51)Int.Cl. H01J 37/073

(21)Application number : 08-080050

(22)Date of filing : 02.04.1996

(71)Applicant : DENKI KAGAKU KOGYO KK

(72)Inventor : TERUI YOSHINORI
TSUNODA KATSUYOSHI

(54) THERMAL FIELD EMISSION CATHODE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a thermal emission cathode with a long life, high reliability, easy operating capability by using cubic system and/or tetragonal system zirconium oxide as the supply source of zirconium and oxygen.

SOLUTION: A thermal field emission cathode has a needle electrode prepared by forming a cover layer comprising zirconium and oxygen on a tungsten single crystal whose axial orientation is <100>. In the thermal field emission cathode, at least one element selected from 2A group elements or 3A group elements is added to zirconium oxide to form solid solution, and thereby, cubic system zirconium oxide, which is stable phase to repeated temperature rising and falling, and/or tetragonal system zirconium oxide, which is metastable phase, are/is formed to prevent the coming off of a reservoir.

CLAIMS

[Claim(s)]

[Claim 1]The thermal electric field radiation negative pole characterized by a supply source of said zirconium and oxygen being zirconium oxide of a cubic and/or ****** in the thermal electric field radiation negative pole which has the needlelike electrode which provided an enveloping layer which becomes a tungsten single crystal in which axial orientation consists of <100> directions from a zirconium and oxygen.

[Claim 2]The thermal electric field radiation negative pole according to claim 1, wherein zirconium oxide is a cubic.

[Claim 3]The thermal electric field radiation negative pole according to claim 1 or 2, wherein zirconium oxide contains at least one or more sorts of elements chosen from 2A fellows and 3A fellows.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the thermal electric field radiation negative pole used as an electron beam source of an electron microscope, an electron-beam-exposure machine, an electron beam tester, a measuring machine, etc.
[0002]
[Description of the Prior Art]In order to acquire a recent years more high-intensity electron beam, the thermal electric field radiation negative pole using the needlelike electrode of the tungsten single crystal is used. Axial orientation this thermal electric field radiation negative pole for the tungsten single crystal chip (henceforth W chip) which consists of <100> directions. It is what provided the enveloping layer (henceforth a ZrO enveloping layer) which consists of a zirconium and oxygen, and reduced the work function of the field (100) of a tungsten single crystal to about 2.8 eV by this ZrO enveloping layer, Since only the minute crystal face equivalent to the field (100) formed in the tip part of said W chip serves as an electron emission area, a high-intensity electron beam is acquired rather than the conventional hot cathode, and, moreover, it has the long lasting feature. It is more stable than cold field emission cathode, operates also with a low degree of vacuum, and has the feature of being easy to use.
[0003]As the thermal electric field radiation negative pole is shown in drawing 1, the W chip 1 which emits an electron beam to the position of the tungsten wire 3 provided in the metal support 5 fixed to the insulating insulator 4 adheres by welding etc., It comprises the suppresser electrode 2 for forming the electric field which controls radiation of the thermal electron from said tungsten wire 3 grade.
[0004]In a part of W chip 1, as shown in drawing 2, the supply source 6 of a zirconium and oxygen, i.e., a reservoir, is formed. Although not illustrated, the surface of the W chip 1 is

covered by the ZrO enveloping layer. Since energizing heating of the W chip 1 is carried out by the tungsten wire 3 and it is used under about 1800K temperature, the ZrO enveloping layer of said W chip 1 surface is exhausted by evaporation. However, since a zirconium and oxygen are spread and the surface of said W chip 1 is continuously supplied from said reservoir 6, a ZrO enveloping layer is maintained as a result.

[0005]The method of passing through the following three processes as the conventional method of forming said ZrO enveloping layer and attaining low work function-ization is publicly known. Namely, the 2nd process of adding an organic solvent etc. to the powder bodies of the precursor zirconium hydride of a 1st process:zirconium inclusion, making it slurry form, making it adhering to W chip of <100> directions, and forming ****** of zirconium hydride : under a high vacuum, W chip is heated, zirconium hydride is decomposed into a zirconium and hydrogen, W chip is heated in the oxygen environment about [of making W chip surface diffusing a zirconium] 3rd process:10 $^{-6}$Torr, and a ZrO enveloping layer is made to form on W chip surface -- it comes out. (Refer to U.S. Pat. No. 4,324,999 gazette)

[0006]

[Problem(s) to be Solved by the Invention]In the conventional thermal electric field radiation negative pole, the crack went into the reservoir repeatedly [of the rising and falling temperature under actual use conditions], when excessive, the reservoir was omitted, and the problem that the life of the thermal electric field radiation negative pole became remarkably short as a result was produced. For this reason, in the actual use of the thermal electric field radiation negative pole, without if possible carrying out rising and falling temperature, once avoiding carrying out rising and falling temperature frequently and setting up operating temperature, the actual condition had provided restriction in that handling so that operating temperature might be maintained.

[0007]However, when manufacturing and adjusting electron beam apparatus, the rising and falling temperature of the multiple times of the thermal electric field radiation negative pole is unavoidable, and. At the time of actual use, the rising and falling temperature of multiple times is not avoided for apparatus maintenance, it may result in a temperature fall in an instant according to the trouble which is not expected, and the thermal electric field radiation negative pole from which a reservoir is not omitted was desired.

[0008]It was made in view of this problem, and repeated rising and falling temperature is borne, a reservoir is not omitted easily, and, as a result, this invention is a long life, and is reliable, and it aims at providing the thermal electric field radiation negative pole which is moreover excellent in operativity.

[0009]

[Means for Solving the Problem]In the thermal electric field radiation negative pole which has the needlelike electrode in which this invention provided an enveloping layer to which axial

orientation becomes a tungsten single crystal which consists of <100> directions from a zirconium and oxygen, It is the thermal electric field radiation negative pole, wherein a supply source of said zirconium and oxygen is zirconium oxide of a cubic and/or ******, and is related with said thermal electric field radiation negative pole especially characterized by said zirconium oxide being a cubic. This invention relates to the aforementioned thermal electric field radiation negative pole, wherein said zirconium oxide contains at least one or more sorts of elements chosen from 2A fellows and 3A fellows.

[0010]

[Embodiment of the Invention]In the conventional thermal electric field radiation negative pole, this inventions acquire knowledge that zirconium oxide results from the volume change of the zirconium oxide produced by the phase transition of the monoclinic system and ****** accompanying rise and fall of temperature and omission of said reservoir arise, and result in this invention.

[0011]Although zirconium oxide usually belongs to a monoclinic system, if temperature is raised from a room temperature, a phase transition will be made ****** in the 1300K neighborhood. At this time, it is accompanied by about 4.6% of volume change. For this reason, when rising-and-falling-temperature operation is repeated to the reservoir which consists of zirconium oxide, itself may break, or a reservoir may separate from a boundary with a needlelike electrode, and may produce what is called omission.

[0012]By making at least one or more sorts of elements chosen from 2a fellows or 3a fellows add and dissolve to zirconium oxide in this invention. The cubic zirconium oxide of a stable phase and/or the tetragonal zirconium oxide of a metastable phase are made to form to a repetition of rising and falling temperature, and omission of said reservoir are prevented.

[0013]Although it is desirable that it is a service temperature field (1400-1800K) of the thermal electric field radiation negative pole, and is cubic zirconium oxide of a heat stable phase, the tetragonal zirconium oxide of a metastable phase can also be used for the zirconium oxide in this invention, and even if both live together, it does not interfere.

[0014]Said cubic zirconium oxide or tetragonal zirconium oxide can be easily obtained by adding at least one or more sorts of elements chosen from 2a fellows or 3a fellows. With a zirconium source like zirconium hydride, distribute to an organic solvent and at least one or more sorts of elements chosen from 2a fellows or 3a fellows For example, [slurry form and nothing], The method of applying this to a needlelike electrode and heating under oxygen environment after an appropriate time, It is the method of mixing and heating at least one or more sorts of elements beforehand chosen from 2a fellows or 3a fellows to zirconium oxide, obtaining a cubic and/or tetragonal zirconium oxide, making this powdered, and applying to a needlelike electrode, etc.

[0015]As an example of at least one or more sorts of elements chosen from 2a fellows or 3a

fellows, Magnesium, yttrium, calcium, cerium, etc. are raised, and since calcium and yttrium dissolve so much to zirconium oxide and tend to obtain cubic zirconium oxide, they are [among these] preferred. Two or more sorts of said element can be combined, and it can also be used.

[0016]In this invention, about the addition of at least one or more sorts of elements chosen from said 2a fellows or 3a fellows. When it is above-mentioned calcium, 8-20-mol% is good at calcium oxide conversion, and although what is necessary is just to choose with reference to a constitutional diagram, since cubic zirconium oxide is especially obtained at a low temperature at 15-20-mol% of case, it is suitable.

[0017]Hereafter, this invention is explained still in detail using an example and a comparative example.

[0018]

[Example]

[Example]After fixing the tungsten wire 3 to the insulating insulator 4 by spot welding at the metal support 5 by which low attachment was carried out, The W chip 1 which cut the single crystal tungsten small-gage wire of <100> directions in pieces was attached to said tungsten wire 3 by spot welding, and further, electrolytic polishing of the tip of the W chip 1 was carried out, it was considered as the sharp tip, and the thermal electric field radiation negative pole intermediate was obtained.

[0019]Isoamyl acetate was ground on the mortar to carrier fluid, the cubic zirconium oxide powder and the commercial zirconium hydride powder which, on the other hand, obtained the zirconium oxide which added the calcium oxide 20% of the weight by heating it for 3 hours by 1800K were mixed, and the slurry was obtained.

[0020]Said slurry is applied to the approximately central position of the tungsten wire 3 of said thermal electric field radiation negative pole intermediate, After it carries out preliminary formation of the reservoir 6 and isoamyl acetate evaporates, it energizes to the tungsten wire 3 in the ultrahigh vacuum of $1x10^{-9}$Torr, the W chip 1 is heated to 1800K, and the pyrolysis of the zirconium hydride is carried out to a zirconium and hydrogen, and the reservoir 6 is calcinated and it solidifies. It heated by bottom of oxygen environment $3x10^{-6}$Torr for 20 hours, oxidation of the zirconium in the reservoir 6, calcination, and diffusion were carried out, and the ZrO enveloping layer was formed in the surface of the W chip 1.

[0021]About the thermal electric field radiation negative pole obtained in the above-mentioned procedure, energizing heating and cooling (stop of energization) were repeated under the ultrahigh vacuum of $1x10^{-9}$Torr, and the state of the reservoir 6 was observed. Although the above-mentioned experiment was repeated 5 times, as shown in Table 1 in any case, it is after 200 heating cooling repetition, and the problem was not produced.

[0022]Apart from what was used for the above-mentioned evaluation, the five thermal electric field radiation negative poles were produced in the above-mentioned procedure, it actually carried in the scanning electron microscope, and the number of occurrence and the life of heating cooling under an actual use situation were investigated. This result is shown in Table 2.

[0023]

[Table 1]

		リザーバ原料	加熱冷却反復回数	リザーバ観察結果
実施例	1	水素化ジルコニウム＋酸化カルシウム２０重量％含有酸化ジルコニウム	２００	異常無し
	2		２００	異常無し
	3		２００	異常無し
	4		２００	異常無し
	5		２００	異常無し
比較例	1	水素化ジルコニウム	３２	脱落
	2		５６	脱落
	3		１２	脱落
	4		４５	脱落
	5		２３	脱落

[0024]

[Table 2]

		リザーバ原料	加熱冷却反復回数	寿命（時間）
実施例	1	水素化ジルコニウム＋酸化カルシウム２０重量％含有酸化ジルコニウム	１６５	６２１０
	2		２３０	８０９０
	3		３１２	１１０１０
	4		１５６	８４２０
	5		２８２	７０５０
比較例	1	水素化ジルコニウム	３５	２０１０
	2		５１	１６８０
	3		２３	５９２０
	4		４５	２８５０
	5		３２	１９５０

[0025][Comparative example] Except on the other hand having used the slurry which consists only of zirconium hydrides as a comparative example, when the same evaluation as an example was performed about the thermal electric field radiation negative pole produced in the same procedure as said example, heating cooling number of occurrence is 12 to 56 times, and the phenomenon in which a reservoir was omitted was accepted. This result was shown in Table 1. The number of times of heating cooling and the life which are carried in a actual scanning electron microscope as well as an example were evaluated, and the result was shown in Table 2.

[0026]

[Effect of the Invention]It is in ** that there are no omission of a reservoir, and it is conventionally stabilized from an example compared with elegance even if it receives the thermal electric field radiation negative pole of this invention repeatedly [heating cooling], and a long life is attained.

[0027]By this invention, omission of a reservoir are prevented repeatedly [of heating cooling], etc., and it operates to rear-spring-supporter stability for a long period of time, and is long lasting, and since the reliable thermal electric field radiation negative pole with little the dispersion is moreover provided easily, it is effective as an electron source of various kinds of electron beam apparatus.

[Translation done.]

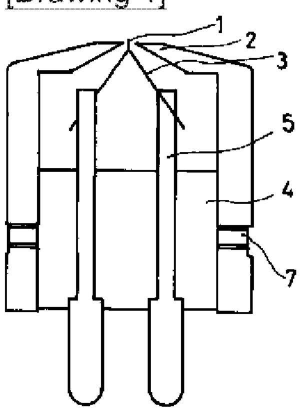
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]The sectional view of the thermal electric field radiation negative pole.
[Drawing 2]The enlarged drawing of W chip of Drawing 1, and the portion of a tungsten wire.
[Description of Notations]
1 : W chip
2 : suppresser electrode
3 : tungsten wire
4 : insulating insulator
5 : metal support
6 : reservoir
7 : the screw for immobilization

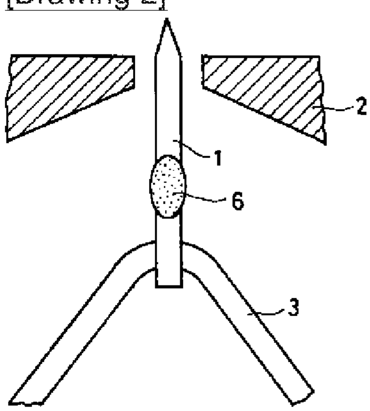
[Translation done.]

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]